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THE STATISTICAL METHOD IN CHEMICAL GEOLOGY.

By F. W. CLARKE.

(Read April 18, 1906.)

In an essay upon the relative abundance of the chemical elements, published some sixteen years ago,¹ I attempted to apply the statistical method to ascertaining the average composition of the earth's crust. . Since that time the data have been repeatedly revised, both by myself and by others, and the results obtained have found applications which I did not anticipate. The composition of the lithosphere has furnished, so to speak, a sort of base-line to which other computations could be referred; the figures, therefore, have acquired a peculiar importance, and it has become desirable to determine, more critically than heretofore, the degree of their validity. To discuss the nature of the averages and to consider how far they may be utilized is the purpose of the present communication. In order to accomplish this purpose I must restate, very briefly, the main points of the original argument.

As a first step in the discussion, it was necessary to assume a definite mass of matter as available for statistical analysis. That mass included the atmosphere, the ocean and a certain portion of the lithosphere; the portion, namely, that may be supposed to lie within our reach. For the last item it was assumed that a shell having a thickness of ten miles below sea-level would represent known material; in other words, that it would consist of rocks essentially identical in general character with those which we can study at the surface. How much thicker the rocky crust of the earth may be is another question, upon which we do not need to enter. It is only the *known* material which concerns us now; and some of that is brought to us by volcanoes from depths far below any to which we can penetrate directly. The eruptive rocks enable us to determine what sort of matter lies below the immediately observable surface.

¹ *Bull. Philos. Soc. Washington*, vol. 11, p. 131, Oct. 26, 1889. Also in U. S. Geol. Survey Bull. 78, p. 34.

I am indebted to Dr. R. S. Woodward for data relative to the volume of matter which is thus taken into account. The volume of the ten-mile rocky crust, including the mean elevation of the continents above the sea, is 1,633,000,000 cubic miles; and to this material we may assign a mean density not lower than 2.5, nor much higher than 2.7. The volume of the ocean is put at 302,000,000¹ cubic miles, and I have given it a density of 1.03, which is a trifle too high. The mass of the atmosphere, so far as it can be determined, is equivalent to that of 1,268,000 cubic miles of water, the unit of density. Combining these data, we get the following expression for the composition of the known matter of our globe.

	Density of Crust. 2.5.	Density of Crust. 2.7.
Percentage of atmosphere.....	.03	.03
Percentage of ocean.....	7.08	6.58
Percentage of solid crust.....	92.89	93.39
	<hr/> 100.00	<hr/> 100.00

In short, we can regard the surface layer of the earth, to a depth of ten miles, as consisting very nearly of 93 per cent. solid and 7 per cent. liquid matter, treating the atmosphere as a small correction to be applied when needed.² The figure thus assigned to the ocean is probably a little too high, but its adoption makes an allowance for the fresh waters of the globe, which are too small in amount to be estimable directly. Their insignificance may be inferred from the fact that a section of the ten-mile crust having the surface area of the United States, represents only about 1.5 per cent. of the entire mass of matter under consideration. Even the mass of Lake Superior thus becomes a negligible quantity.

The composition of the ocean is easily determined from the data

¹ Sir John Murray, *Scottish Geograph. Mag.*, 1888, p. 39, estimates the volume of the ocean at 323,722,150 cubic miles. Karstens, more recently, puts it at 1,285,935,211 cubic kilometres, or 307,496,000 cubic miles. "Eine neue Berechnung der mittleren Tiefen der Oeane," *Inaug. Diss.*, Kiel, 1894. Karstens gives a good summary of previous estimates, which vary widely. To change the figure given in my original essay would be a straining after unattainable precision.

The adoption of Murray's figure for the volume of the ocean would raise its percentage to from 7.12 to 7.88, according to the density, 2.5 or 2.7, assigned to the lithosphere.

given by Dittmar in the Report of the Challenger Expedition.¹ The maximum salinity observed by him amounted to 37.37 grammes of salts in a kilogramme of water, and by taking this figure instead of a lower average value, we can allow for saline masses enclosed within the solid crust of the earth, and which would not otherwise appear in our final estimates. Combining this datum with Dittmar's figures for the average composition of the oceanic salts, we get the second of the subjoined columns. Other elements, contained in sea water, but only in minute traces, need not be considered here. No one of them could reach 0.001 of 1 per cent.

Composition of Salts.		Composition of Ocean.	
NaCl	77.76	O	85.79
MgCl ₂	10.88	H	10.67
MgSO ₄	4.74	Cl	2.07
CaSO ₄	3.60	Na	1.14
K ₂ SO ₄	2.46	Mg14
MgBr ₂22	Ca05
CaCO ₃34	K04
	100.00	S09
		Br008
		C002
			100.00

It is worth while at this point to consider how large a mass of matter these oceanic salts represent. The *average* salinity of the ocean is not far from 3.5 per cent.; its mean density is 1.027, and its volume is 302,000,000 cubic miles. The specific gravity of the salts, as nearly as can be computed, is 2.25. From these data it can be shown that the volume of the saline matter in the ocean is a little over 4,800,000 cubic miles, or enough to cover the entire surface of the United States, excluding Alaska, 1.6 miles deep. In face of these figures, the beds of rock salt at Stassfurt and elsewhere, which seem so enormous at close range, become absolutely trivial. The allowance made for them by using the maximum salinity of the ocean instead of the average, is more than sufficient; for it gives them a total volume of 325,000 cubic miles. That is, the data used for computing the average composition of the ocean, and its average

¹In Volume 1, "Physics and Chemistry."

significance as a part of all terrestrial matter, are maxima; and tend therefore to compensate for the omission of factors which could not well be estimated directly.

The average composition of the lithosphere is very nearly that of the igneous rocks alone. The sedimentary rocks represent altered igneous material, from which salts have been leached into the ocean, and to which oxygen, water and carbon dioxide have been added from the atmosphere. For these changes, corrections can be applied, and their magnitude and effect, as will be shown later, is surprisingly small. The thin film of organic matter upon the surface of the earth can be neglected altogether. In comparison with the ten-mile thickness of rock below it, its quantity is too small to be considered. Even beds of coal are negligible, for their volume also is relatively insignificant. Practically, we have to consider at first, only ten miles of igneous rock; which, when large enough areas are studied, averages much alike in composition all over the globe. This point was established in my original memoir, in which groups of analyses, representing rocks from different regions, were compared. The essential uniformity of the averages was unmistakable, and it has been still further emphasized by later computations by others as well as by myself. The following averages are now available for comparison.

A. My original average of 880 analyses, of which 207 were made in the laboratory of the U. S. Geological Survey and 673 were collected from other sources. Many of these analyses were incomplete.

B. The average of 680 analyses from the records of the Survey laboratories, plus some hundreds of determinations of silica, lime and alkalis. The Survey data up to January 1, 1897.

C. The average of 830 analyses from the Survey records, plus some partial determinations. The Survey data up to January 1, 1900.

D. An average of all the analyses, partial or complete, made up to January 1, 1904, in the laboratories of the Survey.¹

E. An average, computed by A. Harker,² of 397 analyses of

¹ See U. S. Geological Surv. Bull. 228, p. 17, for details.

² *Geol. Mag.*, 1899, p. 220.

igneous rocks from British localities. Many of these analyses were incomplete, especially with respect to phosphorus and titanium.

F. An average of 1,811 analyses, from Washington's tables.¹ Calculated by H. S. Washington. The data represent material from all parts of the world.

Now, omitting minor constituents, which rarely appear except in the more modern analyses, these averages may be tabulated together, although they are not absolutely comparable. The comparison assumes the following form:

	A. Clarke.	B. Clarke.	C. Clarke.	D. Clarke.	E. Harker.	F. Washington.
SiO ₂	58.59	59.77	59.71	60.91	58.75	58.239
Al ₂ O ₃	15.04	15.38	15.41	15.28	15.64	15.796
Fe ₂ O ₃	3.94	2.65	2.63	2.63	5.34	3.334
FeO	3.48	3.44	3.52	3.46	2.40	3.874
MgO	4.49	4.40	4.36	4.13	4.09	3.843
CaO	5.29	4.81	4.90	4.88	4.98	5.221
Na ₂ O	3.20	3.61	3.55	3.45	3.25	3.912
K ₂ O	2.90	2.83	2.80	2.98	2.74	3.161
H ₂ O at 100°	1.9641	2.23	.363
H ₂ O above 100°		1.51	1.52	1.49		1.428
TiO ₂53	.60	.73		1.039
P ₂ O ₅22	.21	.22	.26	.02	.373
	99.66	99.14	99.22	100.61	99.56	100.583

Although these six columns are not very divergent, there are differences between them which may be more apparent than real. Differences of summation are partly due to the omission of minor constituents; but the largest variations are attributable to the water. In two columns hygroscopic water is omitted; in two it is not distinguished from combined water; in two a discrimination is made. By rejecting the figures for water and recalculating to 100 per cent., the averages become more nearly alike, as follows:

¹ U. S. Geological Surv. Professional Paper 14, p. 106.

	A. Clarke.	B. Clarke.	C. Clarke.	D. Clarke.	E. Harker.	F. Washington.
SiO ₂	59.97	61.22	61.12	61.71	60.36	58.96
Al ₂ O ₃	15.39	15.75	15.77	15.48	16.07	15.99
Fe ₂ O ₃	4.03	2.71	2.69	2.68	5.48	3.37
FeO	3.56	3.53	3.60	3.50	2.46	3.93
MgO	4.60	4.51	4.46	4.18	4.20	3.89
CaO	5.41	4.93	5.02	4.94	5.12	5.28
Na ₂ O	3.28	3.69	3.63	3.49	3.34	3.96
K ₂ O	2.97	2.90	2.87	3.02	2.83	3.20
TiO ₂56	.54	.61	.74	.12	1.05
P ₂ O ₅23	.22	.23	.26	.02	.37
	100.00	100.00	100.00	100.00	100.00	100.00

Of these averages, only "D" and "F" need be considered any further, for they include the largest masses of trustworthy data. "A" was only a preliminary computation, "B" and "C" are included under "D"; Harker's average contains too many imperfect analyses. "D" and "F," however, are not strictly equivalent. Washington's average relates only to analyses which were nominally complete, and made in many laboratories by very diverse methods. My average represents the homogeneous work of one laboratory, and includes, moreover, many partial determinations. For the simpler salic rocks determinations of silica, lime and alkalis are generally all that is needed for petrographic purposes. The femic rocks are mineralogically more complex, and for them full analyses are necessary. The partial analyses, therefore, chiefly represent salic rocks, and their inclusion in the average tends to raise the percentage of silica and to lower the proportions of other elements. The salic rocks, however, are more abundant than those of the other class, and so the higher figure for silica seems more probable. This conclusion is in line with a criticism by Mennell,¹ who thinks that the femic rocks received excessive weight in my earlier averages. Mennell has studied the rocks of southern Africa, where granitic types are predominant; and he believes that the true average should approximate to the composition of a granite. A wider range of

¹ *Geol Mag.*, ser. 5, vol. 1, p. 263. For other discussions of the data given in my former papers, see De Launay, *Revue Gén. des Sciences*, April 30, 1904; and Ochsensius, *Zeitsch. prakt. Geol.*, May, 1898.

observation would probably modify that opinion, which, however, is entitled to some weight.

So far, my final average has only been partly given; the minor constituents of the rocks remain to be taken into account. In the laboratory of the Geological Survey the analyses of igneous rocks have been unusually elaborate, and many things have been determined which are too often ignored. The complete average is given in the next table, with the number of determinations to which each figure corresponds. In the elementary column, hygroscopic water does not appear; but an allowance is made for a small amount of iron which was reported in the analysis as FeS_2 . When a "trace" of anything is recorded, it is arbitrarily reckoned as 0.01 per cent., and when a substance is known to be absent from a rock, by actual determination of the fact, it is assigned zero value in making up the averages.

	Number.	Average.	Reduced to 100.	In Elementary Form	
SiO_2	1,358	60.91	59.87	O	47.09
Al_2O_3	912	15.28	15.02	Si	28.23
Fe_2O_3	961	2.63	2.58	Al	7.99
FeO	962	3.46	3.40	Fe	4.46
MgO	1,027	4.13	4.06	Mg	2.46
CaO	1,215	4.88	4.79	Ca	3.43
Na_2O	1,268	3.45	3.39	Na	2.53
K_2O	1,265	2.98	2.93	K	2.44
$\text{H}_2\text{O} -$	770	.41	.40	H17
$\text{H}_2\text{O} +$	832	1.49	1.46	Ti43
TiO_2	870	.73	.72	Zr026
ZrO_2	185	.03	.03	C14
CO_2	469	.53	.52	P11
P_2O_5	884	.26	.26	S11
S	575	.11	.11	Cl07
Cl	234	.07	.07	F02
F	73	.02	.02	Ba089
BaO	617	.11	.11	Sr034
SrO	520	.04	.04	Mn084
MnO	899	.10	.10	Ni023
NiO	243	.03	.03	Cr034
Cr_2O_3	246	.05	.05	V02
V_2O_3	40	.03	.03	Li01
Li_2O	550	.01	.01		
					100.000
		101.74	100.00		

In this computation the figures for C, Zr, Cl, F, Ni, Cr and V are only very rough approximations. They show, however, that these elements exist in igneous rocks in determinable quantities. The elements not included in the calculation represent minor corrections, to be applied whenever the necessity for doing so may arise. For estimates of their probable amounts, the papers by Vogt¹ and Kemp² can be consulted. It is probable that no one of them would reach 0.01 per cent. The elements not mentioned in the table cannot amount to more than 0.5 per cent. altogether; and even that small figure is likely to be an overestimate.

	Shale. A.	Sandstone. B.	Limestone. C.
SiO ₂	58.38	78.66	5.19
Al ₂ O ₃	15.47	4.78	.81
Fe ₂ O ₃	4.03	1.08	} .54
FeO	2.46	.30	
MgO	2.45	1.17	7.90
CaO	3.12	5.52	42.61
Na ₂ O	1.31	.45	.05
K ₂ O	3.25	1.32	.33
H ₂ O at 110°	1.34	.31	.21
H ₂ O above 110°	3.68	1.33 ³	.56 ³
TiO ₂65	.25	.06
CO ₂	2.64	5.04	41.58
P ₂ O ₅17	.08	.04
S09
SO ₃65	.07	.05
Cl		trace	.02
BaO05	.05	none
SrO	none	none	none
MnO	trace	trace	.05
Li ₂ O	trace	trace	trace
C, organic81
	100.46	100.41	100.09

Before we can finally determine the composition of the lithosphere, the sedimentary rocks must be taken into account; and to do this we must ascertain their relative quantity. First, however, we may consider their composition, which has been determined by

¹ *Zeitsch. prakt. Geol.*, 1898, pp. 225, 314, 377, 413, and 1899, pp. 10, 274.

² *Science*, Jan. 5, 1906, and *Economic Geology*, vol. 1, pp. 207.

³ Includes organic matter.

means of composite analyses. That is, instead of averaging analyses, average mixtures of many rocks were prepared,¹ and these were analyzed once for all. The results appear in the preceding table.

A. Composite analyses of 78 shales; or more strictly, the average of two smaller composites, properly weighted.

B. Composite analysis of 253 sandstones.

C. Composite analysis of 345 limestones.

In attempting to compare these analyses with the average composition of the igneous rocks, we must remember that they do not represent definite substances, but mixtures shading into one another. The average limestone contains some clay and sand, the average shale contains some calcium carbonate. Furthermore, they do not cover all of the products derived from the decomposition of the primitive rock, for the great masses of sediments on the bottom of the ocean are left out of account. The analyses of the latter are too few to give conclusive averages, but the data published in the Challenger Reports² indicate a difference between them and the terrigenous deposits. The "red clay," for example, which covers 51,500,000 miles of the ocean floor, at its greatest depths, is much richer in iron than the average shale. In twenty-one analyses of this sediment a mean of 13.61 per cent. of ferric oxide was found. The thickness of this deposit is quite unknown. There are also metamorphic rocks to be considered, such as amphibolites and serpentines; although their quantities are presumably too small to seriously modify the final averages. They might, however, help to explain a deficiency of magnesium which appears in the sedimentary analyses. Partly on account of these considerations, and partly because the sedimentary rocks contain water and carbon dioxide which have been added to the original igneous material, we cannot recombine the composite analyses so as to exactly reproduce the composition of the primitive matter. To do this it would be necessary also to allow for the oceanic salts, which represent, in part at least, losses from the land; but that factor in the problem is perhaps the least

¹ These mixtures were prepared by G. W. Stose, under the direction of G. K. Gilbert. The analyses were made by H. N. Stokes in the laboratory of the U. S. Geological Survey. See Bull. 228, p. 20.

² "Volume on Deep Sea Deposits," p. 198.

embarrassing. Its magnitude is easily estimated, and it gives a measure of the extent to which the igneous rocks have been decomposed.

If we assume that all of the sodium in the ocean was derived from the leaching of the primitive rocks, and that the average composition of the latter is correct, it is easy to show that the marine portion is very nearly one thirtieth of that contained in the ten-mile lithosphere. That is, the complete decomposition of a shell of igneous rock, one third of a mile thick, would yield all the sodium in the ocean. Some sodium, however, is retained by the sediments, and the analyses show that it is about one third of the total amount. That is, the oceanic sodium represents two thirds of the decomposition, and the estimate must, therefore, be increased one half. On this basis, a rocky shell one half mile thick, completely enveloping the globe, would slightly exceed the amount needed to furnish the sodium of the sea and the sediments. No probable change in the composition of the lithosphere can modify this estimate very considerably; and since the ocean may contain primitive sodium, not derived from the rocks, the half mile must be regarded as a maximum allowance. If the primeval rocks were richer in sodium than those of the present day, a smaller mass of them would suffice; if poorer, more would be needed to account for the salt in the sea. Of the two suppositions, the former is the more probable; but neither assumption is necessary. If, however, we assume that our igneous rocks are not altogether primary, but that some of them represent re-fused or metamorphosed sedimentaries, we must conclude that they have been partly leached and have, therefore lost sodium. That is, the original matter was richer in sodium, and the half-mile estimate is consequently too large.

From another point of view, the thinness of the sediments can be simply illustrated. The superficial area of the earth is 199,712,000 square miles, of which 55,000,000 are land. According to Geikie,¹ the mean elevation of all the continents is 2,411 feet. Hence, if all of the land now above sea level were spread uniformly over the globe, it would form a shell about 660 feet thick. If we

¹ "Textbook of Geology," 4th ed., vol. 1, p. 49.

assume this matter to be all sedimentary, which it certainly is not, and add to it any probable allowance for the sediments at the bottom of the sea, we shall still fall far short of the half-mile shell, which, on chemical evidence, is a maximum. In the following calculation this maximum will be taken for granted.

The relative proportions of the different sedimentary rocks within the half-mile shell can only be estimated approximately. Such an estimate is best made by studying the average igneous rock, and determining in what way it can break down. A statistical examination of about 700 igneous rocks, which had been described petrographically, leads to the following rough estimate of their mean mineralogical composition:

Quartz	12.0
Feldspars	59.5
Hornblende and pyroxene.....	16.8
Mica	3.8
Accessory minerals.....	7.9
	<hr/> 100.0

The average limestone contains 76 per cent. of calcium carbonate, and the composite analyses of shales and sandstones correspond to the subjoined percentages of component minerals:

	Shale.	Sandstone.
Quartz ¹	22.3	66.8
Feldspars	30.0	11.5
Clay ²	25.0	6.6
Limonite	5.6	1.8
Carbonates	5.7	11.1
Other minerals	11.4	2.2
	<hr/> 100.0	<hr/> 100.0

If now we assume that all of the igneous quartz, 12 per cent., has become sandstone, it will yield 18 per cent. of that rock, which is evidently a maximum. Some quartz has remained in the shales. One hundred parts of the average igneous rock will form, on decomposition, less than 18 parts of sandstone.

The igneous rocks contain, as shown in the last analysis cited,

¹ The total percentage of free silica.

² Probably sericite in part. In that case the feldspar figure becomes lower.

4.79 per cent. of lime. This would form 8.55 per cent. of calcium carbonate, or 11.2 per cent. of the average limestone. But at least half of the lime has remained in the other sediments, so that its true proportion can not reach 6 per cent., or one third the proportion of the sandstones. The remainder of the igneous material, plus some water and minus oceanic sodium, has formed the siliceous residues which are grouped under the vague title of shale. Broadly, then, we may estimate that the lithosphere, within the limits assumed in this memoir, contains 95 per cent. of igneous rock, with 5 per cent. of sedimentaries. If we assign 4.0 per cent. to the shales, 0.75 per cent. to the sandstones, and 0.25 per cent. to the limestones, we shall come as near to the truth as is possible with the present data.¹ On this basis, the average composition of the lithosphere may be summed up as follows. The analyses of the sedimentary rocks are recalculated to 100 per cent.:

	95 Per Cent. Igneous.	4 Per Cent. Shale	0.75 Per Cent. Sandstone	0.25 Per Cent. Limestone.	Average.
SiO ₂	59.87	58.10	78.33	5.19	59.79
Al ₂ O ₃	15.02	15.40	4.77	.81	14.92
Fe ₂ O ₃	2.58	4.02	1.07	.54	2.63
FeO	3.40	2.45	.30	3.33
MgO	4.06	2.44	1.16	7.89	3.98
CaO	4.79	3.11	5.50	42.57	4.82
Na ₂ O	3.39	1.30	.45	.05	3.28
K ₂ O	2.93	3.24	1.31	.33	2.96
H ₂ O	1.86	5.00	1.63	.77	1.98
TiO ₂72	.65	.25	.06	.71
ZrO ₂0303
CO ₂52	2.63	5.03	41.54	.74
P ₂ O ₅26	.17	.08	.04	.25
S1109	.10
SO ₃64	.07	.05	.02
Cl0702	.07
F0202
BaO11	.05	.0510
SrO0404
MnO1005	.09
NiO0303
Cr ₂ O ₃0505
V ₂ O ₃0302
Li ₂ O0101
C8003
	100.00	100.00	100.00	100.00	100.00

¹ Van Hise, "A Treatise on Metamorphism," U. S. G. S. Monograph 47, p. 940, divides the sedimentary rocks into 65 per cent. shales, including all pelites and psephites, 30 per cent. sandstones, and 5 per cent. limestones.

The final average differs from that of the igneous rocks alone, only within the limits of uncertainty due to experimental errors, and the assumptions made as to the relative proportions of the sedimentaries. If the work were ideally exact, the last column of figures should differ from the first symmetrically, being higher in water and carbon dioxide and lower in all other constituents. Lime and potash, however, show small gains, which are abnormal, and indicative to some extent of the errors above mentioned. It is possible that excessive weight has been assigned to the limestones, but on that theme it is hardly worth while to speculate. The values chosen for the sediments are approximations only, and nothing more can be claimed for them. They seem to be near the truth; as near as we can approach with data which are necessarily imperfect, and so they may be allowed to stand without further emendation.

Now, with the help of this new average, we are in a position to compute the relative abundance of the chemical elements in all known terrestrial matter. For this purpose, the column is restated in elementary form, with an arbitrary allowance of 0.5 per cent. for all of the elements not specifically included in it. As for the atmosphere, it is represented in the final result by 0.02 per cent. of nitrogen, which is a little too low. The mean composition of the lithosphere, the ocean and the atmosphere, then, is as follows:

	93 Per Cent. Lithosphere.	7 Per Cent Ocean	Average, Including Nitrogen.
Oxygen	47.07	85.79	49.77
Silicon	28.06	26.08
Aluminum	7.90	7.34
Iron	4.43	4.11
Calcium	3.44	.05	3.19
Magnesium	2.40	.14	2.24
Sodium	2.43	1.14	2.33
Potassium	2.45	.04	2.28
Hydrogen22	10.67	.95
Titanium4039
Carbon20	.002	.18
Chlorine07	2.07	.21
Bromine008
Phosphorus1110
Sulphur11	.09	.10
Barium0909
Manganese0707
Strontium0303
Nitrogen02
Fluorine0202
All other elements.	.5050
	100.00	100.00	100.00

It would be foolish to ascribe any high degree of accuracy to these figures, for the data are confessedly of very unequal value. They do show, however, clearly and conclusively, the order of magnitudes with which we have to deal. We may claim to know, for example, that oxygen forms about one half of all known terrestrial matter and silicon about one fourth. Next in order of abundance comes aluminum, then iron, and then calcium, followed by magnesium, sodium and potassium in nearly equal proportions. So much is established, and we are also able to say that certain other elements appear in minor, but determinable, amounts. In its general drift, the table is satisfactory; but its details are subject to revision. The question now is, what legitimate uses can be made of it? What problems can it help us to solve?

My answers to these questions, I fear, can hardly be satisfactory. The more closely I scrutinize the uses which have been made of the averages, the more questionable I find them to be. For instance, it is possible to compute from the average chemical or mineralogical composition of the igneous rocks their average physical properties; and as the component data in such a calculation are usually quantities of similar magnitude, the results obtained will probably be quite near the truth. Mr. W. H. Emmons,¹ for example, has determined, from one of my averages, the average mineralogical composition to which it corresponds, using for that purpose the norms of the new quantitative classification. Then, from the known coefficients of expansion of the minerals, he has calculated the mean coefficient for the igneous crust of the earth. The value found is 0.0000199, and its uncertainty cannot be very large. But, after all, what can be done with the figure? If we use it to discuss the swellings and shrinkings of the lithosphere, we are limited to surface phenomena alone, in which the disturbances due to cracks and crevices in the rocks are exceedingly large. If we go below the surface, to a point where the rocks are presumably continuous, this particular coefficient of expansion ceases to be applicable, for it has been modified by changes in temperature and by increased pressure. In other words, our constant is only a constant under

¹ In Chamberlin and Salisbury's "Geology," vol. 1, p. 546.

surface conditions, and at five or ten miles below the surface it must assume a different and unknown value. The coefficient becomes larger as the temperature rises, but the influence of increased pressure is undetermined. In short, the data as they stand to-day are inapplicable to discussions of this kind; although it is conceivable that future discoveries may enable us to eliminate the difficulties that now exist. When the physical properties of rocks and minerals shall have been measured under widely differing conditions of temperature and pressure, we may be able to apply the data to such averages as I have given; and so assist in the solution of geophysical problems.

Professor Van Hise¹ has attempted to combine my third average for the igneous rocks with the composite analyses of the sedimentaries, in order to determine the redistribution of the elements during the processes of metamorphism. In so doing he has assumed that shales, sandstones and limestones exist respectively in the proportions of 65, 30 and 5 per cent. of the sedimentary rocks; and upon recombining the data with allowances for matter contained in the ocean, he found various excesses and deficiencies. These differences from the parent rock he seeks to explain; but it seems to me that his efforts are premature. The data are not yet sufficiently precise to justify so elaborate a discussion, as a comparison of Mr. Washington's average with mine will show. Furthermore, as I have already observed, several important factors in the problem remain to be determined. The metamorphosed sediments and the oceanic deposits are not covered by the composite analyses, and that relative to the shales is otherwise imperfect. It represents only 78 rocks, a number which is quite inadequate. A much larger amount of more varied material must be studied before the analyses of the igneous and sedimentary rocks can be well fitted together. Only the broadest relations are ascertainable now, as I have sought to show in the preceding pages. We can determine, roughly, the *maximum* relative mass of the sedimentaries, and also something of their proportional quantities; but much farther than that we are hardly yet ready to go. One suggestion, however, merely as a sug-

¹ "A Treatise on Metamorphism," pp. 947-1002.

gestion, may be worth considering. The quantity of carbon dioxide locked up within the lithosphere is, as shown by the data now before us, about equal to twenty-five times the mass of the atmosphere. To that quantity must be added at least three more atmospheres, and perhaps a much larger quantity of oxygen which has been consumed in transforming the ferrous compounds of the igneous rocks into the ferric oxide of the sediments. We may well ask whether all of this material was actually absorbed from the atmosphere, and if so, whence was it derived? Did the primeval atmosphere contain it all at once, or was it drawn from cosmical sources, or expelled first from the earth's interior? These questions I shall not attempt to answer, for I do not care to enter the realm of speculation. It is enough for me to point out the order of the quantities involved in the problems thus suggested, problems which have been the themes of many writers, and leave them as crude data for possible future use.

One other phase of geochemical statistics remains to be mentioned; namely, the attempt to use chemical evidence in the measurement of geological time. At least two such efforts have been made; the one by T. Mellard Reade,¹ the other by Professor Joly.² Mr. Reade, from a study of the soluble substances contained in the surface waters of England and Wales, estimates that their removal from the rocks and soil would lower the level of those countries at the rate of one foot in 12,978 years. This means a transfer to the ocean of dissolved matter alone equivalent to 143.5 tons per annum from each square mile of land; and to this must be added the solid sediments. From various data relative to the drainage basins of Europe, and to some large rivers in other parts of the world, Reade calculates that the average denudation of all the land of the globe amounts to about 800 tons annually per square mile. This figure, combined with the supposition that the sediments represent a thickness of ten miles, gives a period of 526,000,000 years since the process of sedimentation began. The assumed thickness is evidently many times too great, and the figure is, therefore, excessive.

¹ "Chemical Denudation in Relation to Geological Time," London, 1879.

² *Sci. Trans. Royal Dublin Soc.*, ser. 2, vol 7, p. 23. Also a note in *Chem. News*, vol. 83, p. 301.

In another calculation, Reade has estimated that the limestones are equal in bulk to a zone 528 feet thick completely enveloping the globe. Then, from the rate at which lime salts are carried from the land into the sea, he computes the time required to form the limestones as equal to 600,000,000 years. I may note here, in passing, that if my own estimate of the mass of the limestones is correct, this quantity should be divided by four, giving 150,000,000 years as the time needed for their formation. I do not care now to criticize Reade's calculations in detail, for his data were in many respects defective, and the conjectural element in his reasoning was very large. In spite of these obvious objections, however, Reade's work has shown certain statistical possibilities, and has pointed out a line of investigation that may be profitably followed. Previous to the appearance of Reade's memoir the mechanical sediments had been used in estimating geological time, but the dissolved matter, which is of nearly equal importance and much more easily measurable, was neglected.

Professor Joly's line of attack upon the time problem was analogous to Reade's, but different. Taking as his fundamental datum the quantity of sodium in the ocean, and then estimating the annual amount of sodium brought in by waters from the land, he was able to compute the time required for the oceanic accumulation. This method of calculation is simple, direct and clear, provided the rate of supply has been constant, and that all corrections are known and applied. Uncorrected, the time needed for the observed accumulation is 99,400,000 years, which is evidently a maximum. Corrected, by a questionable allowance for pre-sedimentary sodium in the ocean, and for cyclic salts lifted by winds from the sea and returned to it again, the estimate is reduced to 89,300,000 years. If we admit that Joly's data are correct, we may round off his figures to between ninety and one hundred millions of years, and feel reasonably confident that the time of sedimentation is a quantity of that order.¹

There are two weak points in Joly's calculation. First, the mag-

¹ For discussions of Joly's memoir see Mackie, *Trans. Edin. Geol. Soc.*, vol. 8, p. 240; Fisher, *Geol. Mag.*, 1900, p. 124; Ackroyd, *Chem. News*, vol. 83, p. 265; 84, p. 56; and *Geol. Mag.*, Aug. and Oct. 1901. See also Sollas, "The Age of the Earth," p. 21.

nitudes of his corrections are uncertain, and secondly, our knowledge of the contribution made by rivers to the sea is most imperfect. Joly has used Sir John Murray's estimate of the composition of river water,¹ and that rests upon insufficient data. Murray has averaged together the analyses of nineteen rivers, which are not named, but which were presumably, for the most part, European. Data are lacking for the great African and Asiatic rivers, the Nile excepted, and the other available material is incomplete. A river varies in composition from time to time and from place to place; so that a single analysis of it may be misleading in the highest degree. And yet many of the published analyses are of that character; that is, they represent single samples of water from river systems in which the local and annual variations may be very large. Furthermore, Murray's average is mainly, if not wholly, of waters from the temperate zone; from which, in all probability, tropical and arctic waters may differ considerably. I speak thus advisedly, for I have compared, and reduced to uniform standards, more than a hundred analyses of river waters, and have noted their wide variations. For a very few streams the average annual composition is known, and from such averages, weighted in accordance with the areas drained, the final estimate must be made. The data are now being gathered; the nature of the work to be done is well understood, and in a few years it may be possible to replace Murray's average with one of a more definite character. Then, and not till then, can Joly's method be profitably applied to the discussion of geological time. His results may or may not be seriously modified, but the conclusions reached will be more definite than any we can attain to now. At all events, the present rate of chemical denudation is a measurable quantity, and it will form an important statistical datum for use in the investigation of various problems.

In conclusion I may be permitted to urge upon chemists and geologists the importance of the statistical method in the investigation of large geochemical problems. The method is evidently applicable in many cases, and leads to conclusions of positive value. We need, however, better material to work with than we have now,

¹ *Scottish Geographical Magazine*, 1887, p. 76.

and I have indicated some of the desiderata. From chemical evidence we can draw deductions relative to the volumes and masses of the sediments, and also gain something towards the measurement of geological time. Even if the conclusions to be reached by these methods are not final, they are at least helpful. In order to be convincing, the chemical evidence must follow lines convergent with other testimony, and when it does so we may be satisfied that we are approaching the truth.